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Electronic supplementary information (ESI)

A single chain magnet involving hexacyanoosmate

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Section 1. Experimental Section

1. Materials and General Procedures.

All chemicals were of reagent grade and used as purchased. Schiff base, $H_2acacen [1]$, [Mn(acacen)Cl] [2], $K_4Os(CN)_6$ [3] and $(Ph_4P)_3[Os(CN)_6]$ [4] were prepared accordingly literature procedures. Elemental analyses were performed on a "Euro-Vector 3000" analyzer. Scimitar FTS 2000 spectrometer was used to record the IR spectra (nujol).

2. Synthesis of (Ph₄P)₂[Mn(acacen)Os(CN)₆](H₂O)_{1.5}(C₃H₇O)_{0.7}(1).

A solution of $[Mn(acacen)(MeOH)_2]PF_6$ (0.05 mmol) in methanol (1 mL) was added to a solution of $(Ph_4P)_3[Os(CN)_6]$ (68,2 mg) in ethanol (2 ml). Ph_4PPF_6 , precipitated from the reaction mixture was centrifuged and discarded. A mother liquor was diluted with i-propanol (2 mL) and this solution was left in the dark during one week. The deep brown block crystals were filtered, rinsed with a small amount of cold i-PrOH, than with 2 portions of Et₂O and air dried. Yield: 48,5 mg (70 %) (Found: C, 59.27; H 5.05; N, 8.17. $C_{68.1}H_{66.6}OsMnN_8O_{4.2}P_2$ requires C, 59.64; H, 4.89; N, 8.17 %, $v_{CN} = 2081$ and 2063(sh) cm-1 (nujol) see full spectrum below).



Figure S1. IR spectrum of 1 in fluorinated oil.

3. Magnetic mesurements. QD MPMS5XL magnetometer was used for all measurements. Powder samples were used for all magnetic measurements, the crystallites had size of order of 0.35 mm. The sample was placed in a half of gelatine capsule and covered by a drop of nujol to prevent crystallites rotation where it was essential; the field was turned on after cooling the sample below 200 K, to avoid a preferential orientation of grains. For $\chi T(T)$ plot the diamagnetic correction was subtracted: for the sample holder and nujol it was measured separately and scaled, for the sample it was calculated according to Pascal's constants [5].

4. X-ray Crystallography. The diffraction experiment was performed on an Oxford Diffraction Gemini R Ultra CCD diffractometer equipped with micro-source Cu tube. The absorption correction was applied empirically using equivalent reflections [6]. The structure was refined using the model for isostructural Fe-Mn compound (in press) with least square method on $|F|^2$ in anisotropic approximation for non-H atoms using SHELXL-97[7]. Hydrogen atoms were located in idealized positions and refined in isotropic approximation using the riding on pivot model. Crystallographic data and details for structure **1** refinement are given in Table 1S. Hydrogen atoms of hydroxo group of *i*-PrOH molecule and water molecules were not localized from residual electron density map; the *i*-propyl molecule is disordered over 2 close positions with relative weight of 0.3 and 0.4. H₂O molecules occupy their positions with 20, 30 and 40% probability. Bond lengths and bond angles are summarized in Table S2.

Section 2. Supplementary Tables and Figures



Figure S2. ORTEP drawing and the numbering scheme in 1: a) anionic part; b) cationic part. Ellipsoids of 50% probability, hydrogen atoms are not shown for clarity.

Chemical formula	$(C_{18}H_{18}OsMnN_8O_2) \cdot 2(C_{24}H_{20}P) \cdot 1.5(H_2O) \cdot 0.7C_3H_7OH$
M _r	1371.37
Crystal system, space group	Triclinic, P1
Temperature (K)	123.0(2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.2901(3), 15.2869(4), 18.7961(5)
α, β, γ (°)	94.05(0), 110.23(0), 114.38(0)
$V(Å^3)$	3176.50 (513)
Ζ	2
F(000)	1392
Radiation type	Cu Κα
μ (mm ⁻¹)	6.25
Crystal size (mm)	$0.28 \times 0.20 \times 0.12$
Data collection	-
Diffractometer	Xcalibur, Ruby, Gemini ultra
Absorption correction	Empirical (using intensity measurements) based on intensities [4]
T_{\min}, T_{\max}	0.838, 1.000
# of measured, independent and observed $[I > 2\sigma(I)]$ reflections	17549, 11086, 8911
R _{int}	0.054
θ°	3.66–66.65
Range of h, k, l	$h = -15 \rightarrow 15, k = -18 \rightarrow 17, l = -22 \rightarrow 22$
Refinement	-
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.116, 0.97
No. of reflections	11086
No. of parameters	778
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma 2(Fo2) + (0.0867P)2]$ where $P = (Fo2 + 2F_c2)/3$
$\Delta_{\max}, \Delta_{\min} (e \text{ Å}^{-3})$	1.42, -1.16

Table S1. Crystal data, data collection and structure refinement parameters for 1

Bond	Bond length, Å	Bond angle	angle(°)
Os1—C2	2.073(5) ×2	O11—Mn1—O21	91.60 (12)
Os1—C1	2.076(4) ×2	O11—Mn1—N21	175.59 (13)
Os1—C3	2.077(4) ×2	O21—Mn1—N21	92.06 (13)
Os2—C6	2.070(5) ×2	O11—Mn1—N11	92.12 (14)
Os2—C4	2.068(7) ×2	O21—Mn1—N11	175.97 (14)
Os2—C5	2.078(5) ×2	N21—Mn1—N11	84.29 (15)
		O11—Mn1—N6	91.63 (13)
Mn1—N2	2.341(3)	O21—Mn1—N6	92.68 (12)
Mn1—N6	2.294(3)	N21—Mn1—N6	90.66 (14)
Mn1—011	1.898(3)	N11—Mn1—N6	85.68 (14)
Mn1—O21	1.905(3)	011—Mn1—N2	92.41 (12)
Mn1—N11	1.973(2)	O21—Mn1—N2	92.43 (12)
Mn1—N21	1.979(4)	N21—Mn1—N2	84.97 (13)
		N11—Mn1—N2	88.95 (14)
		N6—Mn1—N2	173.39 (13)
Bond angle	angle(°)	Bond angle	angle(°)
C2—Os1—C1	92.20 (15)	C4—Os2—C6	89.04 (19)
C2—Os1—C1	87.80 (15)	C4—Os2—C6	90.96 (19)
C2—Os1—C1	87.80 (15)	C4—Os2—C6	90.96 (19)
C2—Os1—C1	92.20 (15)	C4—Os2—C6	89.04 (19)
C2—Os1—C3	91.29 (15)	C4—Os2—C5	91.0 (3)
C2—Os1—C3	88.70 (15)	C4—Os2—C5	89.0 (3)
C1—Os1—C3	90.93 (15)	C6—Os2—C5	91.79 (18)
C1—Os1—C3	89.07 (15)	C6—Os2—C5	88.21 (18)
C2—Os1—C3	88.71 (15)	C4—Os2—C5	89.0 (3)
C2—Os1—C3	91.30 (15)	C4—Os2—C5	91.0 (3)
C1—Os1—C3	89.07 (15)	C6—Os2—C5	88.21 (18)
C1—Os1—C3	90.93 (15)	C6—Os2—C5	91.79 (18)

Table S2. The coordination environment of Os^{III} and Mn^{III} in 1.



Figure S3. The hexagonal packing of the chains in **1** (a) along {111} and (b) {001} crystallographic directions. Hydrogen atoms and solvent molecules are not shown; c) selected angles in three compounds.



Figure S4. The hydrogen bonding network in **1**. Each Os-centre carries four terminal CN-groups able to accept a hydrogen bond. In **1**, two of four cyanide ligands are sterically hindered by Ph_4P^+ cations and do not participate in hydrogen bonding (HB). The other two cyanides form the *RO*-H···N=C bonds alternatively with *RO*-H, R = i-Pr and H. A *i*-PrOH molecule participates in long HB (O...N 3.041(6) Å) and separates Ph_4P^+ moieties in the *b* direction. A shorter HB is formed by a positionally disordered H₂O molecule (O...N 2.866(3) Å) alternatively belonging to one of the two neighboring chains along the axis *a*. The aqua molecules interlie the Ph_4P^+ cations in the inter-chain space. The oxygen atoms of *SB* ligand do not participate in HB. Hence, there is no a HB network linking neighboring chains.



Figure S5. Local coordination environment in **1** (top) and in $Et_4N[Mn_2(SB)_2(MeOH)_2][Os(CN)_6]$ (down) and a Hamiltonian, describing magnetic interactions in the last. J. Dreiser, K. S. Pedersen, A. Schnegg, K. Holldack, J. Nehrkorn, M. Sigrist, P. Tregenna-Piggott, H. Mutka, H. Weihe, V. S. Mironov, J. Bendix and O. Waldmann, *Chem. Eur. J.*, 2013, **19**, 3693



Figure S6. Estimation of Δ_{ξ} for **1** from the linear part of $\ln(\chi T)(1/T)$. The data at 1 kOe (red) deviate from the fitted straight line below 10 K due to the saturation effect. Low field data saturate at lowest temperatures due to the finite size effect. The estimated average chain length is about 50 Os-Mn chain units from the maximum χT value of 160 cm³K/mol and the Curie constant 3.3 cm³K/mol. ac data (green) and dc low field data (black) differ below 3 K due to the slow relaxation effect. The position of the χT maximum is 7 K and in the model, proposed by Coulon *et all* [9], should be equal to the T* value. In our case, however, the T* value determined from the dynamic susceptibility data is 3.5 K. Such a deviation has already been observed.[10]



Figure S7. Hysteresis loop measured for a powder sample of 1 at 1.8 K using three different field sweep rates.



Figure S8. Frequency dependence of ac susceptibility of 1 with curves fitted according to the generalized Debye model.[11] Following equations were used to simultaneously fit $\chi'(v)$ and $\chi''(v)$ from above figure:

$$\chi = \chi' - i\chi'' = \chi_{\infty} + \frac{\chi_0 - \chi_{\infty}}{1 + (i2\pi\nu\tau)^{1-\alpha}}$$



Figure S9. Time dependence of magnetization relaxation following the field change from 10 to 0 kOe, at constant temperatures: 1.8 (top curve), 1.9, 2.0, 2.1, 2.3, and 2.5 K (bottom curve).

The data were fitted using a stretched exponential decay: $M(t) = M_0 \exp[-(t/\tau)^{1-n}]$. Only data for t > 80s were taken into account because it takes a finite time to switch off the field. In about 60 seconds the field drops linearly from 20 to 0 kOe. The time when the current in the magnet reaches 0 was defined as zero time in the above figure. It was confirmed by an attempt to fit a decay with the offset $(t - t_0)$, and values close to zero were obtained.

Table S3. Results of the generalized Debye model fits. The parameter α may change between 0 (single relaxation time) and 1.

T (K)	τ (s)	α
2.8	10.41(15)	0.163(4)
3.0	3.44(2)	0.158(2)
3.2	0.985(6)	0.159(3)
3.4	0.300(2)	0.152(3)
3.7	0.0607(4)	0.143(3)
4.0	0.01468(7)	0.132(2)
4.3	0.00412(3)	0.126(3)
4.6	0.00132(1)	0.122(4)
5.0	3.51(4)e-4	0.112(4)

References:

[1] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, J. Am. Chem. Soc., 1955, 77, 5820.

- [2] Y. P. Cai, H. Z. Ma, B. S. Kang, C.H. Su, W. Zhang, J. Sun and Y. L. Xiong, *J. Organomet. Chem.*, 2001, 628, 99;
 S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, 1968, 7, 268; M. Green, J. Smith and P.A. Tasker, *Inorg. Chim. Acta*, 1971, 5, 17; L. J. Boucher, V. W. Day, *Inorg. Chem.*, 1977, 16, 1360. N. Bresciani-Pahor, M. Calligaris, G.
- Nardin and L. Randaccio, Acta Crystallogr., Sect. B, 1979, **35**, 2776.
- [3] M. G. Hilfiger, PhD Thesis, Texas A&M University, 2010.
- [4] P. Albores, L. D. Slep, L. M. Baraldo, R. Baggio, M. T. Garland, E. Rentschler, Inorg. Chem. 2006, 45, 2361.
- [5] O. Kahn, Molecular magnetism, Wiley, 1993.
- [6] R. C. Clark, J. S. Reid, Acta Cryst. 1995, A51, 887-897.
- [7] A. Altomare, M. C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G.
- Moliterni, Polidori, G., Spagna, R. J. Appl. Cryst. 1999, 32, 115-119
- [8] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.
- [9] C. Coulon, H. Miyasaka and R. Clérac, in Structure and Bonding, ed. R. Winpenny, Springer, 2006, 163.
- [10] H. Miyasaka, T. Madanbashi, A. Saitoh, N. Motokawa, R. Ishikawa, M. Yamashita, S. Bahr, W. Wernsdorfer, R. Clérac, *Chem. Eur. J.*, 2012, **18**, 3942.
- [11] K. S. Cole, R. H. Cole, J. Chem. Phys. 1941, 9, 341.